A novel method, Spin-State-Selective (S3) HMBC hetero, for accurate measurement of heteronuclear coupling constants is introduced. The method extends the S3 HMBC technique for measurement of homonuclear coupling constants by appending a pulse sequence element that interchanges the polarization in 13C-1H methine pairs. This amounts to converting the spin-state selectivity from 1H spin states to 13C spin states in the spectra of long-range coupled 1H spins, allowing convenient measurement of heteronuclear coupling constants similar to other S3 or E.COSY-type methods. As usual in this type of techniques, the accuracy of coupling constant measurement is independent of the size of the coupling constant of interest. The merits of the new method are demonstrated by application to vinyl acetate, the alkaloid strychnine, and the carbohydrate methyl β-maltoside.